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(54) Catalytic distillation structure

Katalytische Distillationsstruktur

Structure de distillation catalytique

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(56) References cited:
EP-A- 0 466 954 US-A- 3 925 252
US-A- 4 443 559 US-A- 4 471 014

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DescriptionBACKGROUND OF THE INVENTION

5 Field of the Invention

[0001] The present invention relates to a structure which can be used in reactions wherein the reaction and distillation of the reaction system are carried on concurrently using the structure as both catalyst for the reaction and as a distillation structure.

10 Related Art

[0002] Recently a new method of carrying out catalytic reactions has been developed, wherein the components of the reaction system are concurrently separable by distillation, using the catalyst structures as the distillation structures.

15 This method is now generally known as catalytic distillation and any reference to catalytic distillation herein will be taken to mean this method or process. Such systems are described variously in U.S. Patents 4,215,011; 4,232,177; 4,242,530; 4,302,356; 4,307,254; 4,336,407; 4,439,350; 4,443,559; and 4,482,775. U.S. Patent 4,447,668 discloses the dissociation of ethers in a catalytic distillation column. In addition, U.S. Patent Nos. 4,443,559 and 4,250,052 disclose a variety of catalyst structures for this use.

20 [0003] Sulzer European Pat. No. 0396650 discloses a catalytic distillation structure comprising semirigid mesh like walls containing catalyst material and formed into channels which are layered together such that the flow of the channels cross. Sulzer U.S. Pat. No. 4,731,229 discloses a similar packing. Other Sulzer distillation packings are shown in U.S. Pat. No s 4,455,339; 4,497,751; 4,497,752; 4,744,928 and 4,497,735 and UK patents 1,471,442; 1,569,828 and 1,186,647.

25 [0004] The EP-A-0 466 954 describes a catalytic structure, comprising a coiled porous screen, and supported by the layers of the coil, a porous tubular container, oriented vertically or horizontally, with particulate catalytic material.

[0005] The present invention provides a catalytic distillation structure for use in reactions, which can be used as a distillation structure. In order to serve both functions, it has been found that the structure must meet three criteria. First, the structure must be such as to provide for even spatial dispersement in the reactor distillation column. That is, the catalyst structures must rest in the column in a geometric arrangement which will perform the desired functions of reaction and distillation sites. To achieve this the structure must be such as to provide fairly uniform spatial distribution in the column.

30 [0006] A second criteria is that there must be sufficient free space in the catalyst bed to allow for the liquid phase surface contact and vapor phase distillation with the concurrent separation of the material in the column by the distillation into vapor and liquid phases. It has been observed that in the catalyst bed a free space of about 50 volume % is adequate to obtain an operable fractionation.

35 [0007] A third criteria is the necessity for the catalyst bed to be able to expand and contract as it must during use without undue attrition of the catalyst.

[0008] The present invention meets all of the criteria in a superior manner.

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SUMMARY OF THE INVENTION

[0009] Briefly the present invention is a catalytic distillation structure comprising at least one plurality of flexible, semi-rigid open mesh tubular elements filled with a particulate catalytic material (catalyst component) and sealed at both ends, intimately associated with and supported by a mesh screen coiled into a spiral having a longitudinal axis, said tubular element being placed diagonally to the longitudinal axis thereby forming a bale.

45 [0010] The flexible, semi-rigid open mesh tubular element filled with a particulate catalytic material preferably has a fastener every 25 -305 mm (1-12 inches) along the length of the tube to form a multiple link shaped catalytic distillation structure. The links formed by the fasteners may be evenly or irregularly spaced.

50 [0011] The bale shaped catalytic distillation structures are formed by placing at least one tubular element on top of the wire mesh screen, such as demister wire, in a diagonal array, such that when the wire mesh screen is rolled up, the rolled structure provides a new and improved catalytic structure which is particularly useful as a catalytic distillation structure. Further embodiments include multiple stack arrangements of alternating mesh screens and tubular elements that are rolled into a bale shaped structure. The tubular elements on alternating layers are preferably arrayed on the mesh screens in opposite directions such that their paths cross. In this preferred embodiment, each tubular element defines a spiral within the bale.

55 [0012] The catalyst component may take several forms. In the case of particulate catalytic material, generally from 60mm to about 1mm down through powders, the catalytic material is enclosed in a tubular porous container which is

formed from an appropriate material such as screen wire or polymeric mesh. The material used to make the container is preferably inert to the reactants and conditions in the reaction system. The screen wire may be formed from, for example, aluminum, steel, stainless steel, and the like. Particularly suitable materials include open mesh knitted stainless steel wire, known generally as demister wire or an expanded wire or an expanded aluminum. The polymeric mesh may be formed from, for example, nylon, teflon, or the like. Particularly suitable materials include open mesh knitted polymeric filaments of nylon, Teflon and the like.

[0013] The mesh or threads per inch of the material chosen to form the screen wire or polymeric mesh is chosen such that the catalyst is retained within the tubular container and will not pass through the openings in the mesh. Although catalyst particles of about 0.15mm size or powders may be used, particles having a diameter of up to about 6mm (1/4 inch) may be used.

[0014] The tubular container is preferably formed from a resilient material which comprises at least 70 vol% open space up to about 95 vol%. The total volume of open space for the catalytic structure/catalytic distillation structure should be at least 10 vol% and preferably at least 20 vol% up to about 65 vol%. Thus, desirably the resilient material used to form the tubular containers should comprise about 30 vol% to 70 vol% open space.

[0015] The present tubular shaped container may be composed of a wire mesh tube that has been closed by flattening the tube together at one end with a fastener such as staples or other appropriate means such as crimping, welds, or sewn metal, etc. The tube container is then filled with the appropriate catalyst material. The second end of the wire mesh tube is closed in a like manner as the first end, so that the axis of the second closed end is in the same plane as the first closed end. This process may be repeated several times to obtain multiple tubular links filled with a catalyst material.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] FIG. 1 shows one embodiment of the present invention comprising multiple link catalyst distillation structures arrayed on a wire mesh screen.

[0017] FIG. 2 is a side view of the catalytic distillation structure shown in FIG. 1 along line 2-2.

[0018] FIG. 3 shows an alternative embodiment of the present invention comprising a stack arrangement.

[0019] FIG. 4 is a side view of the catalytic distillation structure shown in FIG. 3 along line 4-4.

[0020] FIG. 5 is a close-up view of the sheet of woven wire mesh used in the present invention.

[0021] FIG. 6 shows a tubular element.

[0022] FIG. 7 is a top view of the structure shown in FIG. 1, that has been rolled up to form a bale shaped catalytic distillation structure.

[0023] FIG. 8 is a perspective view of the catalytic distillation structure shown in FIG. 7.

DETAILED DESCRIPTION AND PREFERRED EMBODIMENTS

[0024] Referring to FIG. 6, a wire mesh tube 10 is closed at one point A with a fastener 12, which may be wire, crimping, welds, or sewn metal. The wire mesh tube 10 is then filled with a catalyst component 14 and the second point B is closed by a fastener 12. This filling procedure is repeated several times until the desired number of links are obtained.

[0025] In FIG. 1, the link structure 24 is placed on top of a sheet of demister wire 16. The demister wire 16 can be of any size, thickness, or design, desired to obtain an efficient catalytic distillation. FIG. 5 shows a close-up view of a typical demister wire 16 having interconnected wires 18 to form a wire mesh. Referring to FIG. 1, the link structures 24 are placed on top of the rectangular sheet of demister wire 16, diagonally along the length of the sheet of demister wire 16. Continuous and link tubular elements may be intermixed or all of the tubes in a layer or catalytic distillation structure may be of either type. The invention is illustrated with the preferred link type tubes, however the continuous tubes although not specifically shown are exactly the same as the tubular elements 22 and 24 with the fasteners 12 omitted. The sheet of demister wire 16 is then rolled lengthwise and stapled or otherwise attached to the adjacent portion of the screen along the free edge 28 by staples 26 to create a bale shaped catalytic structure as shown in FIGs. 7 and 8. Although not shown the tubular element may be attached, for example by staples, to the wire screen in order to facilitate manufacture and to insure that the tubes will stay in place throughout their use.

[0026] In FIG. 7 the end of each row of tubular elements 24 is visible. In FIG. 8 the completed bale is shown in perspective view.

[0027] FIG. 3 shows an alternative embodiment of the present invention. A second sheet of demister wire 20 is placed on top of the structure found in FIG. 1, with the multiple link tubular elements 22 placed on top of the first sheet of demister wire 20, in diagonally opposite rows to the tubular elements 24 found on the sheet of demister wire 16.

[0028] The two sheets of demister wire 16, 20, are then rolled together lengthwise toward the inside to create a bale shaped catalytic structure of the same type as shown in FIG's 7 and 8. The internal placement of the multiple link

structures form a spiral arrangement in the bale. Multiple stacks, having different configurations, may be rolled to create any desired bale configuration.

[0029] The continuous tube shaped catalytic distillation structure may be used interchangeably in the same manner as the multiple link shaped structure to create new bale shaped catalytic distillation structures.

5 [0030] The bale shaped structures found in FIG.'s 7 and 8 are ready for insertion into a column suitable for catalytic distillation.

[0031] The bale shaped catalytic distillation structures may be configured in any order within the catalytic distillation column to achieve the results desired. In the place of the wire mesh, equivalent materials made from polymers may be used. In place of staples or sewn seams, adhesives may be used, with the only proviso being that the materials employed withstand attack by the materials and conditions in the reactor distillation column.

10 [0032] The size of catalyst components and the relative amount of the resilient component associated therewith or surrounding the catalyst components will determine the open space in the bed, which should preferably be at least about 10 volume % and more preferably at least 20 volume %. In the case of longer beds, it may be desirable to have a larger open space, thus a larger volume of the resilient material compared to the catalyst component would be employed.

15 [0033] Although the present catalytic distillation structures are especially useful for a process where there is a concurrent reaction distillation, it is also very useful for vapor phase reactions, since the catalyst bed prepared from the present structure provides a very low pressure drop therethrough.

20 [0034] The catalytic material may be any material, appropriate for the reaction at hand, that is, it may be an acid catalyst or a basic catalyst or others such as catalytic metals and their oxides or halides, suitable for a multitude of catalytic reactions and, of course, heterogeneous with the reaction or other fluids in the system. Some specific reactions are:

CATALYST	REACTION
Acid cation exchange resins	dimerization, polymerization, etherification, esterification, isomerization, alkylation
Magnesia, chomia, brucite	isomerization
Molecular sieves (synthetic aluminosilicates)	dimerization, polymerization, alkylation, isomerization, selective hydrogenation, dehydrogenation
Cobalt thoria	Fisher-Tropsch process
Cobalt molybdate	hydrofining

25 [0035] The material for forming the tubular container may be the wire mesh materials, such as stainless steel, expanded aluminum, or the like. Suitable adhesives such as epoxys or various of the hot melt adhesives which are not softened at the temperatures of use or attacked by the reactants or products may be used to join both polymeric materials and wire into the appropriate configuration. Similarly staples, brads or other fastening means may be used. The wire may be sealed by welding. In a similar fashion, seals may be obtained with laser welding on the meltable materials.

30 [0036] The catalytic distillation structure may be individually and randomly placed into a reactor distillation column or arranged in specific patterns or groupings. Moreover, any catalyst bed may be a mixture of various shapes and sizes of the present catalytic distillation structures.

[0037] The invention may be particularly described with reference to the following clauses:

35 1. A catalytic distillation structure comprising a first plurality of flexible, semi-rigid open mesh tubular elements filled with a particulate catalytic material, sealed at both ends, supported by a wire mesh screen coiled into a spiral having a longitudinal axis, said tubular elements being arrayed at an angle to the longitudinal axis.

40 2. The catalytic distillation structure according to Clause 1 wherein the mesh openings in said tubular element are smaller than the diameter of particles of catalyst.

45 3. The catalytic distillation structure according to Clause 1 wherein a second plurality of flexible, semi-rigid open mesh tubular elements filled with a particulate catalytic material, sealed at both ends, intimately associated with and supported by a second wire mesh screen positioned on the first tubular elements, said second tubular elements being arrayed at an angle to the longitudinal axis and opposite to the first plurality of tubular elements.

50 4. A catalytic distillation structure comprising a sheet of wire mesh screen with at least one multiple link tubular

element containing particulate catalytic material placed on top of said screen to form a stack and said stack rolled to form a bale.

5. A catalytic distillation structure comprising a sheet of wire mesh screen with at least one continuous tubular element containing particulate catalytic material placed on top of said screen to form a stack and said stack rolled to form a bale.

Claims

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1. A catalytic structure comprising a coiled porous screen (16) and, located between, and supported by, the layers of the coil, a porous tubular container (10) having particulate catalytic material (14) located therein, the axis of the tubular container being placed diagonally to the longitudinal axis of the coil.

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2. A catalytic structure according to Claim 1 wherein the structure includes a pair of coiled screens (16.20), adjacent layers within the coil being provided by the one and the other respectively of the two screens.

3. A catalytic structure according to Claim 1 or Claim 2 comprising a plurality of porous tubular containers each placed diagonally to the longitudinal axis of the coil.

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4. A catalytic structure according to Claim 3 wherein tubular containers on opposite sides of each layer of the coil are each placed diagonally to the longitudinal axis of the coil and are mutually opposed.

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5. A catalytic structure according to Claim 4 wherein the tubular containers are angled at 90° to one another.

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6. A catalytic structure according to any one of Claims 1 to 5 wherein the tubular container is a multiple link tubular container (22).

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7. A catalytic structure according to Claim 6 wherein the multiple link tubular container is formed by seams or fastenings (12) spaced along the length of the container.

8. A catalytic structure according to any one of Claims 1 to 7 wherein the tubular container is formed from a resilient material, said resilient material being polymeric mesh, wire mesh, stainless steel screen wire or aluminum screen wire.

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9. A catalytic structure according to Claim 8 wherein the resilient material comprises up to 95%, preferably about 30 vol% to 70 vol%, open space.

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10. A catalytic structure according to any one of Claims 1 to 9 wherein the particle size of the catalytic material (14) is in the range of from about 0.15 mm to about 6 mm (1/4 inch).

11. A catalytic structure according to Claim 10 wherein the particle size of the catalytic material (14) is in the range of from about 0.25mm to about 1mm.

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12. A catalytic structure according to any one of Claims 1 to 11 containing from about 10 to 65 vol% open space.

13. A catalytic structure according to any one of Claims 1 to 12 wherein the openings in the tubular containers are smaller in diameter than the diameter of the catalyst particles.

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14. A catalytic distillation structure as claimed in any one of Claims 1 to 13.

Patentansprüche

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1. Katalytische Struktur, umfassend ein spiralförmiges poröses Gitter (16) und einen zwischen den Lagen der Spirale angeordneten und davon getragenen porösen röhrenförmigen Behälter (10), in dem sich teilchenförmiges katalytisches Material (14) befindet, wobei die Achse des röhrenförmigen Behälters diagonal zur Längsachse der Spirale angeordnet ist.

2. Katalytische Struktur nach Anspruch 1, in der die Struktur ein Paar spiralförmige Gitter (16, 20) umfasst, wobei aneinandergrenzende Schichten innerhalb der Spirale durch das eine bzw. das andere der beiden Gitter zur Verfügung gestellt werden.
5. 3. Katalytische Struktur nach Anspruch 1 oder 2, die eine Vielzahl poröser röhrenförmiger Behälter umfasst, die jeweils diagonal zur Langsachse der Spirale angeordnet sind.
10. 4. Katalytische Struktur nach Anspruch 3, in der röhrenförmige Behälter auf gegenüberliegenden Seiten jeder Schicht der Spirale jeweils diagonal zur Längsachse der Spirale angeordnet und einander entgegengesetzt sind.
15. 5. Katalytische Struktur nach Anspruch 4, in der die röhrenförmigen Behälter im Winkel von 90° zueinander liegen.
6. Katalytische Struktur nach einem der Ansprüche 1 bis 5, in der der röhrenförmige Behälter ein mehrgliedriger röhrenförmiger Behälter (22) ist.
20. 7. Katalytische Struktur nach Anspruch 6, in der der mehrgliedrige röhrenförmige Behälter durch Nähte oder Befestigungen (12) gebildet wird, die in Abständen entlang der Länge des Behälters angeordnet sind.
8. Katalytische Struktur nach einem der Ansprüche 1 bis 7, in der der röhrenförmige Behälter aus einem elastischen Material gebildet ist, wobei es sich bei diesem elastischen Material um Polymernetz, Drahtnetz, Gitterdraht aus rostfreiem Stahl oder Gitterdraht aus Aluminium handelt.
25. 9. Katalytische Struktur nach Anspruch 8, in der das elastische Material bis zu 95 %, bevorzugt etwa 30 bis 70 Vol.-%. offenes Volumen aufweist.
10. Katalytische Struktur nach einem der Ansprüche 1 bis 9, in der die Teilchengröße des katalytischen Materials (14) im Bereich von etwa 0,15 mm bis etwa 6 mm (1/4 inch) liegt.
30. 11. Katalytische Struktur nach Anspruch 10, in der die Teilchengröße des katalytischen Materials (14) im Bereich von etwa 0,25 mm bis etwa 1 mm liegt.
12. Katalytische Struktur nach einem der Ansprüche 1 bis 11, die etwa 10 bis 65 Vol.-% offenes Volumen aufweist.
13. Katalytische Struktur nach einem der Ansprüche 1 bis 12, in der der Durchmesser der Öffnungen in den röhrenförmigen Behältern kleiner ist als der Durchmesser der Katalysatortorteilchen.
35. 14. Katalytische Destillationsstruktur nach einem der Ansprüche 1 bis 13.

40. **Revendications**

1. Une structure catalytique comprenant un écran poreux enroulé (16) et, situé entre, et supporté par, les couches de l'enroulement, un conteneur tubulaire poreux (10) ayant un matériau catalytique particulaire (14) disposé dans celui-ci, l'axe du conteneur tubulaire étant placé diagonalement par rapport à l'axe longitudinal de l'enroulement.
45. 2. Une structure catalytique selon la revendication 1, dans laquelle la structure comprend une paire d'écrans enroulés (16, 29), des couches contiguës dans l'enroulement étant fournies par l'un et l'autre respectivement des deux écrans.
50. 3. Une structure catalytique selon la revendication 1 ou la revendication 2 comprenant une pluralité de conteneurs tubulaires poreux, chacun placé diagonalement par rapport à l'axe longitudinal de l'enroulement.
4. Une structure catalytique selon la revendication 3, dans laquelle les conteneurs tubulaires sur les côtés opposés de chaque couche de l'enroulement sont chacun placés diagonalement par rapport à l'axe longitudinal de l'enroulement et sont mutuellement opposés.
55. 5. Une structure catalytique selon la revendication 4, dans laquelle les conteneurs tubulaires font un angle de 90° l'un par rapport à l'autre.

6. Une structure catalytique selon l'une quelconque des revendications 1 à 5, dans laquelle le conteneur tubulaire est un conteneur tubulaire à maillons multiples (22).
- 5 7. Une structure catalytique selon la revendication 6, dans laquelle le conteneur tubulaire à maillons multiples est formé par des joints ou moyens de fixation (12) espacés sur la longueur du conteneur.
8. Une structure catalytique selon l'une quelconque des revendications 1 à 7, dans laquelle le conteneur tubulaire est formé d'un matériau élastique, ledit matériau élastique étant une toile polymère, une toile métallique, une toile en acier inoxydable ou une toile en aluminium.
- 10 9. Une structure catalytique selon la revendication 8, dans laquelle le matériau élastique comprend jusqu'à 95 %, de préférence d'environ 30 % en volume à 70 % en volume d'espace ouvert.
- 15 10. Une structure catalytique selon l'une quelconque des revendications 1 à 9, dans laquelle la dimension particulaire du matériau catalytique (14) se situe dans la gamme d'environ 0,15 mm à environ 6 mm (1/4 pouce).
11. Une structure catalytique selon la revendication 10, dans laquelle la dimension de particule du matériau catalytique (14) se situe dans la gamme d'environ 0,25 mm à environ 1 mm.
- 20 12. Une structure catalytique selon l'une quelconque des revendications 1 à 11 renfermant d'environ 10 à 65 % en volume d'espace ouvert.
13. Une structure catalytique selon l'une quelconque des revendications 1 à 12, dans laquelle les ouvertures dans les conteneurs tubulaires sont d'un diamètre plus petit que le diamètre des particules de catalyseur.
- 25 14. Une structure de distillation catalytique selon l'une quelconque des revendications 1 à 13

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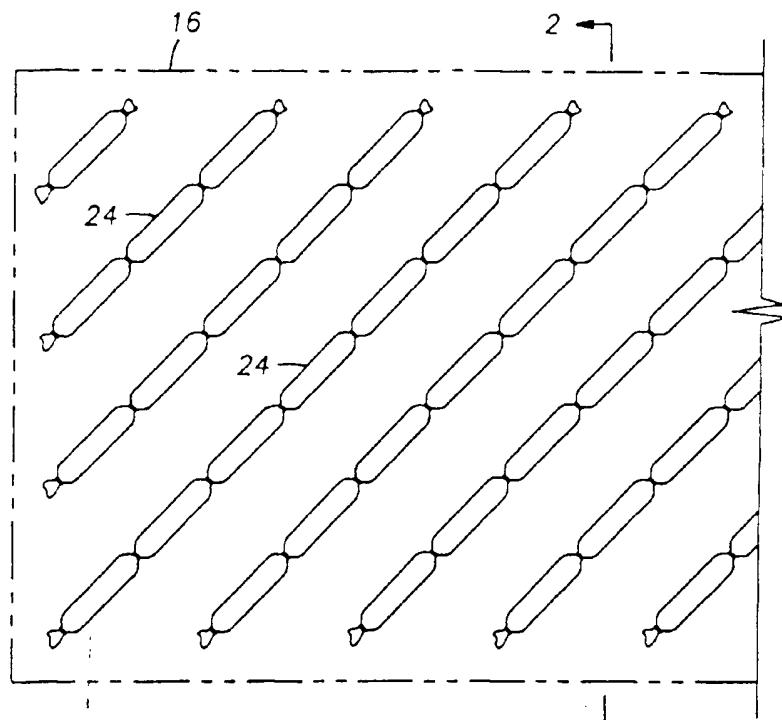


FIG. 1

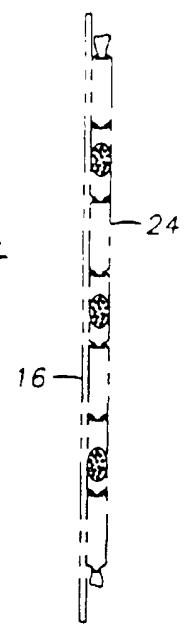


FIG. 2

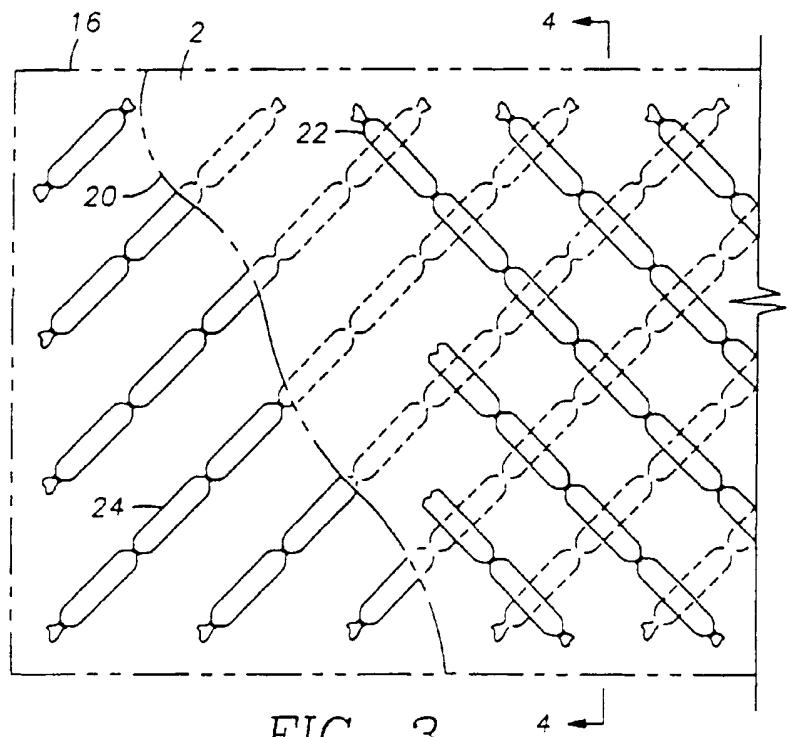


FIG. 3

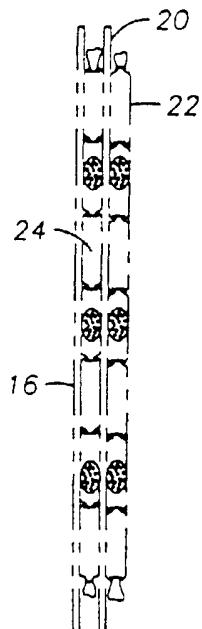


FIG. 4

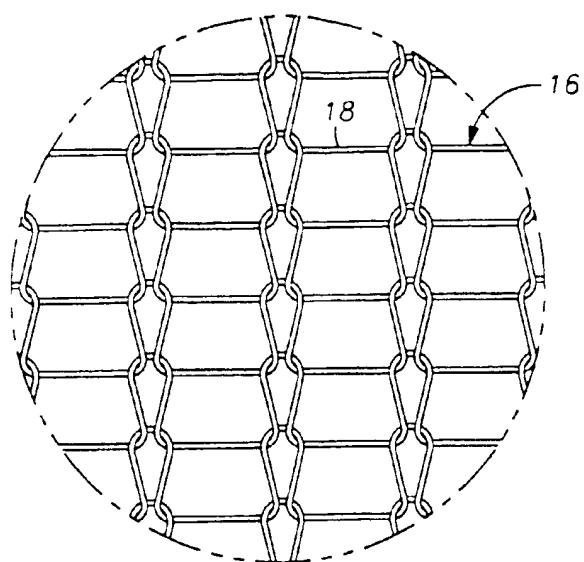


FIG. 5

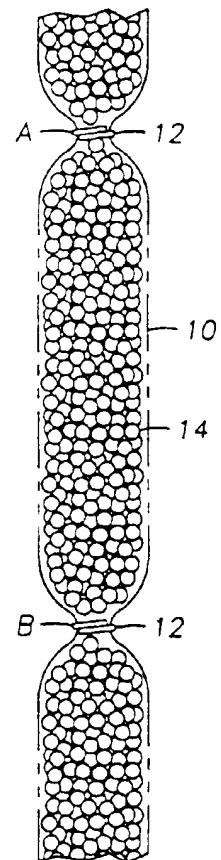


FIG. 6

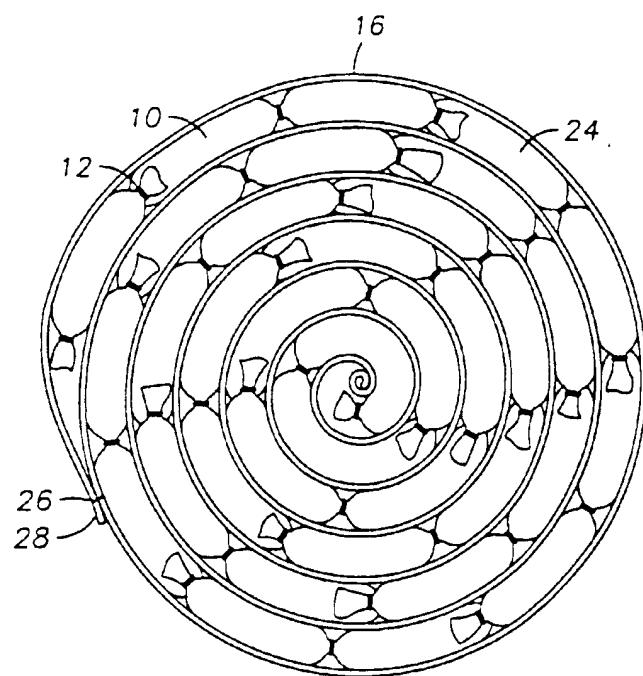


FIG. 7

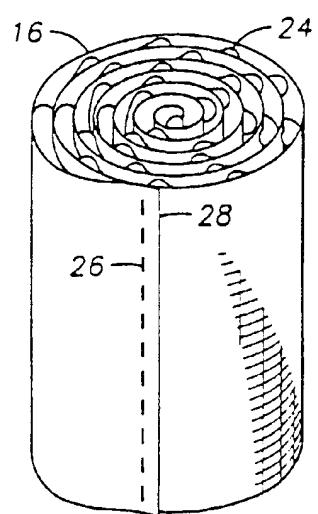


FIG. 8